

SORPTION OF LINEAR ALKYL BENZENE SULFONATES AND SULFOPHENYLCARBOXYLIC ACIDS ON MARINE SEDIMENTS

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ABSTRACT

The sorption of linear alkylbenzene sulfonates (LAS) and of their main biodegradation intermediates, sulfophenylcarboxylic acids (SPC) has been characterized in marine sediments. The required equilibrium time for undecylbenzene sulfonate (C₁₁LAS) sorption is 12 h, and 24 h for sulfophenyl undecanoic acid (C₁₁SPC). C₁₁LAS sorption decreases with temperature due to the exothermic character of this process. C₁₁SPC sorption is less complete and less homogeneous than for C₁₁LAS. The alkylic or carboxylic chain length (C₁₀-C₁₃) is correlated positively with the partition coefficient, and the effect of the carboxylic group is more significant than that of the additional methylene group. Sorption of LAS and SPC homologues (C₁₀-C₁₃) are reversible processes. Desorption of SPC homologues is almost complete, but the desorption percentage of LAS homologue decreases with alkylic chain length. Small fractions of sorbed LAS homologues could take longer to be desorbed than the times covered by this study.

Keywords: linear alkylbenzene sulfonate, sulfophenylcarboxylic acid, sorption, marine sediment, desorption

Introduction

Sorption is a key process in the characterization of the environmental fate of compounds released to the aquatic environment, because it determines their distribution between different compartments. Sorption affects the mobility, and can also affect toxicity and biodegradation of compounds by influencing bioavailability. Sorption of organic pollutants is determined by the molecular structure of the sorbed compound, the properties of the sorbent, and by physico-chemical/environmental conditions (temperature, ionic strength,...). This process is especially relevant for surfactants (González-Mazo et al. 1998), since these compounds present a pronounced tendency to be sorbed onto interfaces.

Linear alkylbenzene sulfonates (LAS) are the most commonly used synthetic anionic surfactant in the formulation of detergents. Commercial LAS comprise a mixture of homologues, differing in function of the length of the alkyl chain (from C₁₀ to C₁₄), and of isomers, which differ in function of the position of the sulfophenyl group link with the alkyl chain. These surfactants are biodegradable in aerobic conditions (Swisher, 1987). In fact even at low temperatures, removal of LAS and their degradation intermediates exceeds 99% during activated sludge treatment and takes place preferentially for long alkyl chain homologues and external isomers (León et al. 2006). However, significant quantities of these compounds enter the marine environment due to their high consumption (in Spain, 5.0 g·inhab⁻¹·day⁻¹) (Berna and Cavalli, 1999). Littoral environments receive direct discharges of treated or non-treated wastewaters or indirect discharges through rivers, where LAS are present, dissolved or associated with particulate material. Consequently LAS have been detected in marine waters, suspended solids and sediments (González-Mazo et al. 1997; Lara-Martín et al. 2006; León et al. 2002); and their biodegradation intermediates, sulfophenylcarboxylic acids (SPCs) have also been detected (Lara-Martín et al. 2006; León et al. 2001, 2002).

Once LAS access the marine environment, degradation and sorption are the most significant processes that affect their removal and transport in this system. Aerobic biodegradation of LAS and SPCs exceeds 99% in seawater at initial concentrations of 1 mg·L⁻¹ (León et al. 2004). C₁₁SPC biodegradation is faster than C₁₁LAS biodegradation, which is an indication that the β -oxidation is a more rapid process than the ω -oxidation. Although biodegradations of the first LAS biodegradation intermediates, SPCs of longer carboxylic chain, are very rapid processes in seawater under aerobic conditions, the presence of these compounds in the marine environment (González-Mazo et al. 1997; Lara-Martín et al. 2006; León et al. 2001, 2002) makes it necessary to study in depth the behavior of SPCs in the environment. Recent research has shown the anaerobic biodegradation of LAS in coastal marine sediments (Lara-Martín et al. 2007), where LAS is mainly sorbed to sediment whereas the less hydrophobic SPCs are predominant in solution. Sorption has special relevance because this process could reduce the bioavailability of these compounds for microorganisms, and consequently also reduce their rate of biodegradation.

The sorption properties of LAS have been studied in fresh (Hand and Williams, 1987; Matthijs and De Henau, 1985; Westall et al. 1999) and marine waters (Fytianos et al. 1998a; Rubio et al. 1996). Numerous experiments have shown that hydrophobic interaction is mainly responsible for LAS sorption on soil or sediments (Hand and Williams, 1987; Rubio et al. 1996; Westall et al. 1999), as shown by the higher sorption

capacity found for homologues of longer alkylic chain or for isomers with longer alkylic fragments. Other studies have shown that the interaction at lower concentrations is specific on sorbent ionic centers due to electrostatic strengths; however at higher concentrations sorption is a hydrophobic process (Ou et al. 1996).

The effect of organic carbon content in sediments on LAS sorption is not clear. The majority of the studies carried out have shown a good correlation between LAS sorption and the organic fraction of sediments (Matthijs and De Henau, 1985; McAvoy et al. 1994; Westall et al. 1999). However this dependency has not been observed (Hand and Williams, 1987; Ou et al. 1996) in tests performed at lower LAS concentrations. Adsorption intensity of LAS is correlated significantly and positively with clay, silt and microcline contents of soils (Ou et al. 1996).

At higher pH levels, LAS sorption is lower on sediments (Di Toro et al. 1990; Fytianos et al. 1998b; Westall et al. 1999) and on the surface of biota (Fernández et al. 1995). On the other hand, LAS sorption increases sharply with salinity (Rubio et al. 1996); consequently this process must take place more readily in seawater than in fresh waters. In seawater, LAS solubility is lower due to the high Ca^{2+} concentration (10^{-2}M) (Cohen et al. 1993; Verge et al. 2001); as a result of this, higher sorption has been detected at increased Ca^{2+} concentrations (Westall et al. 1999).

Available studies on the reversibility of LAS sorption are scarce and contradictory; some authors suggest that it is completely reversible (Hand and Williams, 1987; Westall et al. 1999), and others that it shows notable irreversibility (Matthijs and De Henau, 1985; Rubio et al. 1996). Consequently more studies were needed to complete knowledge on this topic.

The distribution of SPCs has been characterized in several littoral environments (González-Mazo et al. 1997; Lara-Martín et al. 2006; León et al. 2001, 2002), where researchers have detected that SPCs are also associated with suspended solids or sediments but to a less extent compared with LAS. The presence of the carboxylic group in the molecule reduces its hydrophobicity and affects, together with the carboxylic chain length, SPC distribution in the environmental compartments. However, to date, the sorption of SPCs has not been described in any published studies. Hence the sorption of these biodegradation intermediates on sediments needs to be characterized adequately to determine its effect on SPC availability.

This study deals with the sorption of one of the most representative LAS homologues, and of its first biodegradation intermediate, at environmentally

representative concentrations, with lower detection limits than previous studies considering sorption onto container walls. In this investigation, LAS and SPC sorption has been characterized at concentrations ($50\text{--}1000\ \mu\text{g}\cdot\text{L}^{-1}$) similar to those detected in the marine environment, to determine the effect of hydrocarbon chain length and of the presence of the carboxylic group on their sorption on marine sediments. This general aim encompasses the following more specific objectives: i) to determine the time required to reach steady state in the C_{11}LAS and C_{11}SPC sorption process (i.e. to characterize kinetically the C_{11}LAS and C_{11}SPC sorption process); ii) to establish, at different temperatures, the partition coefficients of C_{11}LAS and C_{11}SPCs in marine sediments; iii) to establish partition coefficients of $\text{C}_{10\text{--}13}\text{LAS}$ and $\text{C}_{10\text{--}13}\text{SPC}$ in marine sediments under the same conditions, in order to evaluate the effect of the carboxylic chain length and the presence of the carboxylic group; and iv) to determine the reversibility of LAS and SPC sorption on marine sediments.

EXPERIMENTAL SECTION

Material. Marine water and sediments used in sorption assays were sampled from non-contaminated areas. Water was collected from more than 12 miles off the coast (Gulf of Cádiz), and passed through $45\ \mu\text{m}$ GF/F Whatman filters, sterilized with Millipore Sterivac-GP10 vacuum filtration units ($0.22\ \mu\text{m}$) and maintained at $4\ ^\circ\text{C}$ until use. The main physico-chemical properties of seawater are given in Table 1. Sediment was sampled in a salt marsh from Cádiz Bay without anthropogenic pollution (Table 1). Sediment was dried at $80\ ^\circ\text{C}$, milled and sieved ($300\ \mu\text{m}$ mesh). LAS homologues were donated by PETRESA, and SPCs were synthesized at Cádiz University.

Sorption Experiments. Polypropylene centrifuge tubes of 80 mL volume (Herolab, Wiesloch, Germany) have been used. The specific surface of each tube is $0.0114\ \text{m}^2$. Fifty milliliters of sterile seawater with the desired concentration of LAS or SPC were mixed with 0.5 grams of marine sediment in the centrifuge tubes. These tubes were continuously shaken and maintained at constant temperature in a culture chamber ($\pm 0.2\ ^\circ\text{C}$) and darkness to avoid any microbiological growth. Sorption of LAS and of some of their biodegradation intermediates (SPC) has been characterized, including control tests (without sorbent) in every assay. The dissolved phase was recovered after intense centrifugation (30 min at $20000\ \text{g}$), and was fixed by adding 1mL formaldehyde (35 %) and maintained frozen until analysis.

Table 1. Physicochemical properties of natural seawater and marine sediment used in sorption tests.

| Seawater | | Sediment | |
|------------------------------------|------------------|---|-------|
| Salinity | 36.249 | Organic carbon (%) | 1.47 |
| pH | 8.13 | Organic nitrogen (%) | 0.16 |
| Alkalinity (mM) | 2.43 | PO ₄ ³⁻ (µg·g ⁻¹) | 1.67 |
| HCO ₃ ⁻ (mM) | 2.10 | Fe (%) | 4.05 |
| LAS (mg·L ⁻¹) | n.d. | Mn (µg·g ⁻¹) | 235 |
| PO ₄ ³⁻ (µM) | 0.79 | LAS (µg·g ⁻¹) | <0.05 |
| SiO ₂ (µM) | 27.72 | Specific surface (m ² ·g ⁻¹) | 14.9 |
| NO ₃ ⁻ (µM) | 3.33 | Averaged pore diameter (nm) | 3.5 |
| NO ₂ ⁻ (µM) | 1.14 | Porosity | 0.76 |
| NH ₄ ⁺ (µM) | 0.27 | Clay (%) | 3.0 |
| Ca ²⁺ (M) | 10 ⁻² | Slime/mud (%) | 35.5 |
| SO ₄ ²⁻ (mM) | 29.2 | Sand (%) | 61.5 |
| I (ionic strength, M) | 0.750 | | |
| n.d.: non detected | | | |

Water recovery was higher than 99.3 % for controls without sediment and 98.2 % for samples. These values are higher than those obtained in previous studies (90 % by McAvoy et al., 1994). The amount of LAS or SPC in the sediment was determined by the difference between the initial concentration and that measured in the aqueous phase, taking into consideration the adsorption on the walls of the centrifuge tube, determined using blanks.

In all tests performed (Table 2), two sorption surfaces were considered: plastic walls of the centrifuge tube (polypropylene) and sediment. Both sorption processes have been characterized separately, performing first sorption tests at several concentrations and temperatures without sediment, and later the same experiments with marine sediment.

The time required to reach steady state has been determined for concentrations of 200 µg·L⁻¹ C₁₁LAS or C₁₁SPC at 5 °C, taking samples at 0.5, 1, 2, 4, 6, 8, 12, 24 and

48 h. Sorption isotherms of C₁₁LAS and C₁₁SPC on marine sediment and polypropylene have been obtained at different temperatures (5, 10, 15, 20 and 25 °C) and concentrations (50, 100, 200, 400, 600 and 1000 µg·L⁻¹). In the 5 °C sorption test sorption reversibility was also determined. Desorption tests were performed as a continuation of the sorption tests. When the sorption test had been completed, 50mL seawater (free of any sorbed compounds) was added to the centrifuge tube to quantify LAS/SPC desorption, and the system was characterized once steady state had been reached again.

Table 2. Sorption experiments performed, specifying compounds used, temperatures and concentrations, and which desorption test was performed.

| Compound | Temperature (°C) | Concentration(µg·L ⁻¹) | Desorption test |
|--|-------------------|------------------------------------|-----------------|
| C ₁₁ LAS | 5, 10, 15, 20, 25 | 50, 100, 200, 400, 600, 1000 | Only at 5°C |
| C ₁₁ SPC | 5, 10, 15, 20, 25 | 50, 100, 200, 400, 600, 1000 | Only at 5°C |
| C ₁₀ LAS, C ₁₁ LAS | 15 | 400 | Yes |
| C ₁₂ LAS, C ₁₃ LAS | | | |
| C ₁₀ SPC, C ₁₁ SPC | 15 | 400 | Yes |
| C ₁₂ SPC, C ₁₃ SPC | | | |

Several physico-chemical parameters of the sorption process, such as entropy (ΔS), enthalpy (ΔH) and free energy (ΔG), have been calculated from the variation of steady-state thermodynamic constant (K_o) at infinite dilution with temperature, using the approximation proposed by Biggar & Cheung (1973).

A sorption-desorption test has been performed for LAS and SPC homologues to determine the effect of the hydrocarbon chain length, from 10 to 13 carbon atoms, and of the presence of the carboxylic group on the sorption process and its reversibility (Table 2). This experiment was performed at 15 °C and an initial LAS/SPC concentration of 400 µg·L⁻¹ of each homologue was prepared as already described for the rest of the cases. The applied equilibrium time had been previously determined for the C₁₁LAS and C₁₁SPC experiments, for LAS and SPC homologues respectively.

Analysis of LAS and SPC. Every water sample ($\approx 50\text{mL}$) obtained in the sorption experiments was pre-concentrated by solid phase extraction and subsequently analyzed by HPLC using the specific LAS and SPC method proposed by León et al. (2000). First all samples were adjusted to pH 3 by adding HCl, and were passed through a previously-activated C_{18} column (10mL MeOH and 10mL H_2O at pH 3). The minicolumn was cleaned with 6mL of MeOH/ H_2O (30/70) and eluted with 10mL of MeOH. Subsequently the methanolic extract was dried with heat and N_2 flux, and concentrated to 1mL of MeOH/ H_2O (80/20). Finally the extract obtained was analyzed by HPLC with fluorescence detection (León et al. 2000). Quantification was performed using external standards treated in the same conditions as the samples.

RESULTS AND DISCUSSION

Sorption kinetic of C_{11}LAS and C_{11}SPC

The equilibrium time for LAS sorption experiments is usually less than 6 hours (Fytianos et al., 1998a; Matthijs and De Henau, 1985; Rubio et al. 1996; Westall et al. 1999). However our study has shown that, during this period of time, up to 80-90 % of the sorption process takes place, but that 12 hours are necessary for the stationary state to be reached (Figure 1). Previous studies have applied shorter times in order to prevent LAS biodegradation from occurring, but in our case, primary biodegradation of LAS intermediates has not been detected in sediment assays due to the prior sterilization of the water and sediment used. In the case of C_{11}SPC , 24 h of shaking are required to reach steady state in these conditions (Figure 1). Consequently the times applied in LAS and SPC sorption tests were 12 h and 24 h respectively in all assays. The C_{11}LAS partition coefficient on marine sediment is approximately 15 times higher than the C_{11}SPC partition coefficient at these conditions ($5\text{ }^\circ\text{C}$ and $200\text{ }\mu\text{g}\cdot\text{L}^{-1}$). The presence of the carboxylic group increases the water solubility of this compound and reduces the proportion that is sorbed on sediment.

Sorption Isotherms of C_{11}LAS and C_{11}SPC

In these tests, two sorption surfaces must be taken into account, the polypropylene and the test material, either marine sediment ($10\text{ g}\cdot\text{L}^{-1}$). Both sorption processes have been characterized separately; first tests were performed without sediment to determine sorption on polypropylene (centrifuge tube), and then tests with sediment. In the second group of tests, total sorption is the sum of the sorption on sediment and polypropylene together.

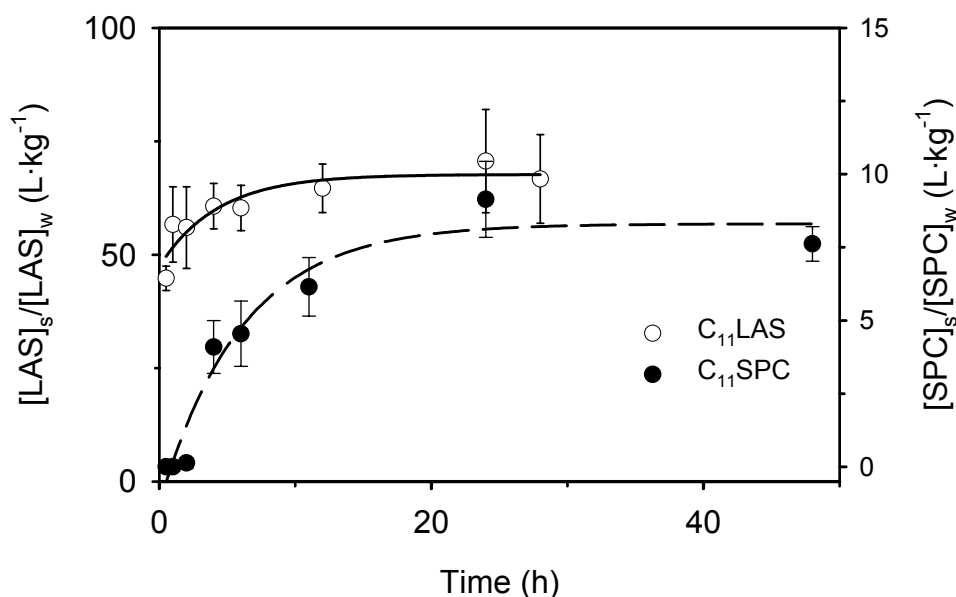


Figure 1. Sorption curve of C₁₁LAS and C₁₁SPC in sediment (200 µg·L⁻¹ and 5 °C).

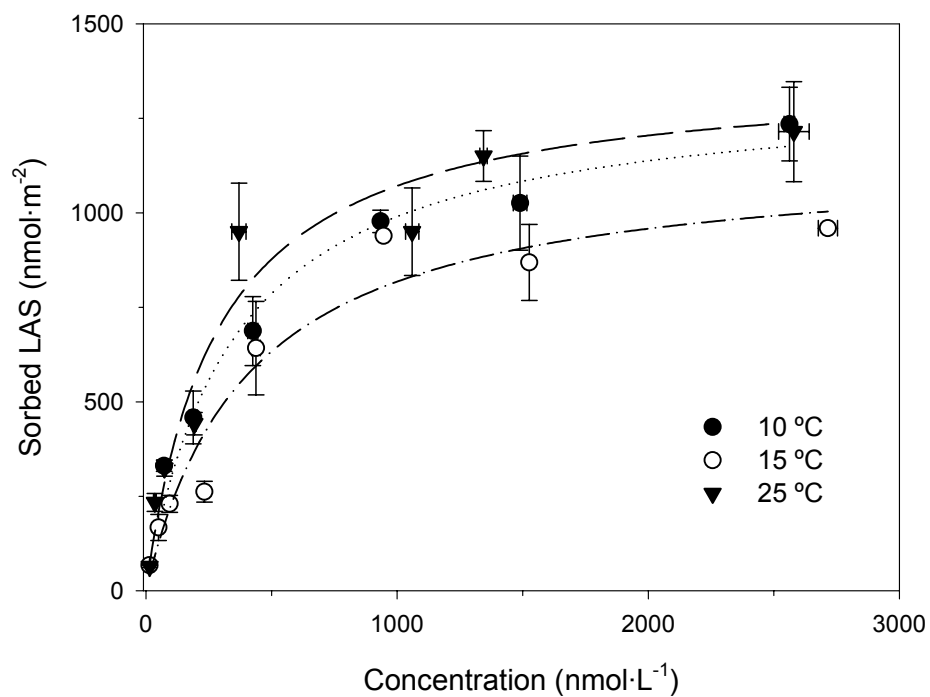
Sorption of C₁₁LAS on polypropylene (centrifuge tube)

Sorption of C₁₁LAS on polypropylene has been characterized by performing tests at the same conditions as for tests with sediment (Figure 2A). The results

obtained have been fitted to a Langmuir isotherm, expressed as:
$$X = \frac{x_{\max} \cdot C}{\frac{1}{k_p} + C}$$

where X is the amount of LAS or SPC adsorbed on polypropylene (µg·m⁻²), C is the concentration in solution (µg/L), x_{\max} and k_p are Langmuir parameters, x_{\max} is the maximum value of analyte adsorption capacity (µg·m⁻²), and k_p is the partition coefficient (L·m⁻²). A Langmuir isotherm has been applied because it is considered that all polypropylene sites are energetically similar and that sorption take place in a single layer. The fits obtained are shown in Figure 2A and the values of the adjustable parameters are given in Table 3.

A



B

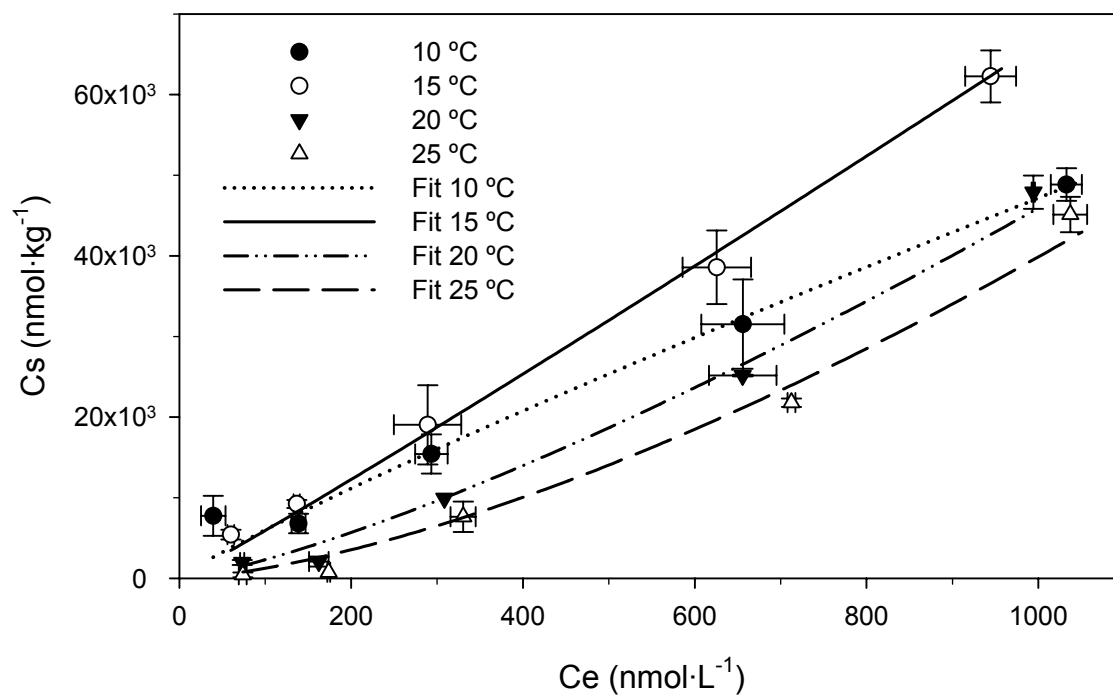


Figure 2. C_{11} LAS sorption isotherms on polypropylene (2 A) and on marine sediments (2 B) at different temperatures, showing fit obtained with Langmuir isotherm model and with Freundlich isotherm model respectively.

Table 3. Parameters of Freundlich isotherm corresponding to C₁₁LAS and C₁₁SPC sorption on marine sediment at different temperatures, and the mean partition coefficient (K_{df}) estimated from Freundlich *k* parameter.

| Compound | Temperature (°C) | <i>k</i> (L·kg ⁻¹) | <i>n</i> | <i>r</i> ² | K _{df} |
|---------------------|------------------|--------------------------------|----------|-----------------------|-----------------|
| C ₁₁ LAS | 10 | 96.600 | 0.896 | 0.997 | 53.0±7.7 |
| | 15 | 47.596 | 1.048 | 0.999 | 63.2±3.6 |
| | 20 | 5.839 | 1.299 | 0.999 | 37.2±12.3 |
| | 25 | 1.223 | 1.504 | 0.998 | 29.3±14.9 |
| C ₁₁ SPC | 5 | 12.050 | 1.079 | 0.987 | 21.8±1.8 |
| | 15 | 0.0002 | 2.340 | 0.990 | 10.3±10.8 |
| | 25 | 1.758 | 1.282 | 0.991 | 14.0±6.1 |

Maximum C₁₁LAS sorption capacity on polypropylene is similar at 10, 15 and 25 °C, with an averaged value of 1289±117 nmol·m⁻² and *k*=0.003±0.001 L·m⁻². These values are similar to those obtained for C₁₂LAS onto polystyrene lattices at 25 °C (Jódar-Reyes et al. 2005). However the experimental values obtained for C₁₁LAS at 5 °C are three times higher (*x*_{max}=4112 nmol·m⁻² and 0.001 L·m⁻²), probably due to a better organization of LAS sorption at lower temperatures, and consequently sorption capacity is higher at these conditions.

Sorption of C₁₁LAS on marine sediment

Sorption on sediment has been calculated by subtracting the portion of LAS sorbed to polypropylene for each equilibrium concentration from total amount of LAS sorbed. The data obtained has been fitted to a Freundlich isotherm: $C_s = k_f \cdot C_e^n$

where *C_s* is the amount of LAS adsorbed on the sediment (nmol·kg⁻¹), *C_e* is the concentration in solution (nmol·L⁻¹), *k_f* is the sorption constant (L·kg⁻¹) and *n* is a measure of the intensity of sorption. A value for *n* below 1 indicates a normal Langmuir isotherm, while *n* above 1 is indicative of a cooperative adsorption (Hand and Williams, 1987). The results obtained for C₁₁LAS sorption on marine sediments at 10, 15, 20 and 25°C and the obtained isotherm fits are shown in Figure 2B. Partition coefficients were

determined from k_f values, considering $k_{df}=C_s/C_e= k_f \cdot C_e^n / C_e = k_f \cdot C_e^{n-1}$.

The parameter k that characterizes the sorption process on sediment, decreases with temperature (Table 3), due to the exothermic character of this reaction. However a simultaneous increase of the parameter n is also observed, associated with the intensity of sorption and dependent on the sorption surface. This variation in n shows that there are two different sorption surfaces, and there are changes in the affinity of the compound sorbed by sediment or polypropylene depending on temperature. As previously commented, higher C_{11} LAS sorption capacity has been detected at 5 °C, and consequently lower sorption on sediment has been observed at these conditions ($k=39.78 \text{ L}\cdot\text{kg}^{-1}$, $n=0.94$ and $r^2=0.985$, $k_{df}=27.9\pm2.2$).

The effect of temperature on LAS sorption has been evaluated by comparing C_{11} LAS mass sorbed onto sediment and onto the centrifuge tube ($\mu\text{g } C_{11}\text{LAS}$) at different temperatures. LAS sorbed on polypropylene increases with concentration until a maximum value (12-15 nmol) is reached, corresponding to the maximum capacity of a monolayer that is constant at higher concentrations, except at 5 °C where this capacity is apparently three times greater. Sorption on sediment increases slightly until a concentration in solution of 600-750 $\text{nmol}\cdot\text{L}^{-1}$ is reached, because sorption take place on both surfaces, and increases notably with LAS concentration at higher values when sorption take place only on the sediment surface. The change in the sorption distribution is due to the maximum polypropylene capacity being reached. Sorption distribution is affected by temperature; in fact sorption on polypropylene is favored at 20 and 25 °C at low concentrations. However sorption is higher on sediment at 5 and 10 °C. This change could explain the variation of n with temperature (Table 3).

The C_{11} LAS partition coefficient (sediment/water) decreases with temperature at lower concentrations. This could be due to LAS sorption on marine sediments being an exothermic process, and so could be favored at lower temperatures, as we will confirm in this article. At low LAS concentrations, the partition coefficient could be higher due to the higher affinity between LAS and the specific sorption points. Once the most favored sorption points have been occupied, the affinity decreases and consequently the partition coefficient detected is lower.

The partition coefficient (K_d) decreases with concentration, a finding previously described by Matthijs and De Henau (1985) in freshwater sediments. Apparently this is not the case at 20 °C and 25 °C because K_d is lower at lower concentrations. However, this is probably due to the higher affinity of C_{11} LAS for the polypropylene surface at

these conditions. In fact if we assumed that all the sorption of C₁₁LAS took place on sediment, we would not be able to detect differences with temperature for experiments performed at initial concentrations higher than 1200 nmol·L⁻¹. Total sorption (polypropylene+sediment) is very similar at 20 and 25 °C for all concentrations; consequently the distribution between phases shows less difference with concentration at higher than at lower temperatures.

Sorption of C₁₁SPC on polypropylene and marine sediment

C₁₁SPC is not sorbed on polypropylene, and on sediment it is sorbed less, and less homogeneously, than its LAS counterpart. C₁₁SPC is a less hydrophobic molecule than C₁₁LAS due to the presence of the carboxylic group in the molecule structure, and for this reason, its sorption is favored less than that of C₁₁LAS. As has been observed for C₁₁LAS, C₁₁SPC sorption is favored slightly more at 5 °C, although there is no clear effect of temperature on the sorption process (Table 3).

Reversibility of C₁₁LAS and C₁₁SPC sorption

Our results show that LAS sorption is a reversible process (Table 4), as other authors have indicated previously (Hand and Williams, 1987; Westall et al. 1999). Consequently, LAS is capable of desorbing from marine sediment, even at low LAS concentrations and with the high ionic strength of seawater. The increase of the partition coefficient during desorption has been described previously by Hand and Williams (1987) for C₁₄LAS. The affinity of LAS for active sediment sites tends to decrease with surfactant concentration, due to the most favored sites having already been occupied. It can be concluded that LAS desorption is fast and reversible for the weakly sorbed fractions, but other fractions probably require longer times to be desorbed, as has been observed for other organic compounds in sediments (Cornelissen et al., 1998).

C₁₁SPC desorption performed at 5 °C is almost complete (higher than 75 % at all concentrations), as a consequence of the relatively weak interactions between this molecule and the sorbent surface.

Considering C₁₁LAS and C₁₁SPC sorption as an equilibrium system (LAS↔LAS-sediment) and assuming a first order kinetic, sorption and desorption velocity constants have been determined using the steady state data. The sorption velocity constant is significantly higher for C₁₁LAS (0.84 d⁻¹) than for C₁₁SPC (0.09 d⁻¹), but the desorption constant of C₁₁SPC (1.12 d⁻¹) is slightly higher than the corresponding constant of C₁₁LAS (0.69 d⁻¹). Consequently the presence of the

carboxylic group in the molecule reduces the velocity and the intensity of C₁₁SPC sorption, and favors a faster desorption than that detected for C₁₁LAS.

Table 4. C₁₁LAS sorption and desorption partition coefficients (K_d) and percentage of C₁₁LAS desorbed at 5°C and different concentrations.

| Concentration (nmol·L ⁻¹) | K _d sorption (L·Kg ⁻¹) | K _d desorption (L·Kg ⁻¹) | Desorption (%) |
|--|--|--|-------------------|
| 300 | 40.5 ± 5.1 | 103.9±17.1 | 9.4 |
| 600 | 40.8 ± 7.5 | 85.2±19.7 | 21.5±14.3 |
| 1200 | 41.1 ± 4.8 | 67.2±33.8 | 49.2±19.3 |
| 1800 | 55 ± 5.1 | 65.0±20.6 | 38.9±11.5 |
| 3000 | 41.0 ± 9.3 | 56.8±11.4 | 61.9±5.8 |

Sorption of C₁₀-C₁₃LAS and C₁₀-C₁₃SPC homologues on marine sediment

The effect of alkylic chain length and of the presence of the carboxylic group on sorption has been evaluated by comparing the sorption of C₁₀LAS, C₁₁LAS, C₁₂LAS and C₁₃LAS with the sorption of the corresponding intermediate biodegradation homologues (C₁₀SPC, C₁₁SPC, C₁₂SPC and C₁₃SPC) at the same conditions (Table 5).

The carboxylic group increases molecule polarity thus reducing the presence of sulfophenylcarboxylic acids in the sorbed phase. In fact SPC partition coefficients are much lower than those of the LAS homologues, by a factor of approximately 40 if we assumed that all LAS sorption took place on the sediment (Table 5). The chain length (alkylic or carboxylic) is correlated positively with partition coefficient; the effect of this is that the presence of the carboxylic group of the molecule is more significant than the additional methylene groups. Consequently LAS sorption mechanisms with marine sediments must be basically of the hydrophobic type, as other authors have observed previously in river and marine sediments (Hand and Williams, 1987; Matthijs and De Henau, 1985; Rubio et al. 1996). However, in the case of SPCs, this consequence is not so clear, because the SPC partition coefficient is of the same magnitude for all cases, and it suggests that SPC interactions with sediments could also be site-specific surface interactions.

Table 5. C₁₀₋₁₃LAS and C₁₀₋₁₃ SPC sorption and desorption partition coefficients (K_d), obtained for marine sediment and for sorption on polypropylene at 15°C and 400 µg·L⁻¹. Desorption percentage of each homologue is also included.

| Homologue | Partition coefficient | | | Desorption (%) |
|---------------------|---|--|--|----------------|
| | K _d sediment (L·Kg ⁻¹) | K _d polypropylene (L·m ⁻²) (L·Kg _{sed} ⁻¹)** | K _d sediment desorption (L·Kg ⁻¹) | |
| C ₁₀ SPC | 1±1 | 0 | <0.01* | 90.0* |
| C ₁₁ SPC | 3 ± 2 | 0 | 0.04±0.03* | 80.7* |
| C ₁₂ SPC | 4 ± 4 | 0 | 0.6±0.6* | 75.6* |
| C ₁₃ SPC | 7 ± 4 | 0 | 1.1±0.5* | 62.3* |
| C ₁₀ LAS | 12 ± 5 | 1.4±0.1 (32±3)** | 14 ± 7 | 68.6 |
| C ₁₁ LAS | 62 ± 7 | 2.5±0.1 (56±2)** | 85 ± 3 | 42.0 |
| C ₁₂ LAS | 116 ± 13 | 4.5±0.3 (103±6)** | 312 ± 38 | 19.6 |
| C ₁₃ LAS | 137 ± 38 | 14.6±4.7 (332±108) ** | 391 ± 103 | 13.7 |

*Approximate values due to proximity to the quantification level.

** Partition coefficient of C₁₁LAS on polypropylene considering sorption had taken place on sediment.

Sorption onto the tube walls is relevant for LAS homologues but not for SPCs due to their higher polarity. The LAS sorption partition coefficients are slightly lower than those detected previously in marine sediments by Rubio et al. (1996), probably because those authors did not take into account the container walls as a sorption surface.

Sorption of LAS and SPC homologues (C₁₀-C₁₃) are reversible processes. Desorption of SPC homologues is almost complete, but that of LAS homologues decreases in percentage terms with alkylic chain length. Consequently LAS desorption must be reversible for the weakly sorbed fractions, but other fractions probably require longer times to be fully desorbed (Cornelissen et al., 1998), especially for homologues with stronger sorption interactions (C₁₂LAS and C₁₃LAS).

Thermodynamic parameters for C₁₁LAS and C₁₁SPC sorption

The values obtained for the thermodynamic variables are shown in Table 6. A

decrease of the LAS partition coefficient (equilibrium thermodynamic constant at infinite dilution, K_0) with temperature is observed, and consequently it is an exothermic process.

Table 6. C_{11} LAS thermodynamic sorption parameters, including equilibrium constant at infinite dilution, the correlation coefficient, standard free energy and entropy.

| T (K) | $\ln K_0$ | r^2 | ΔG° (KJ·mol ⁻¹) | ΔS° (KJ·mol ⁻¹) |
|-------|-----------|--------|--|--|
| 278 | 5.1206 | 0.9945 | -11.84 | -0.42 |
| 283 | 5.1361 | 0.9950 | -12.09 | -0.41 |
| 288 | 4.5457 | 0.9998 | -10.89 | -0.41 |
| 293 | 3.2564 | 0.9999 | -7.94 | -0.41 |
| 298 | 1.3858 | 0.9983 | -3.44 | -0.42 |

Sorption enthalpy calculated by fitting $\ln K_0$ to temperature is -127.8 KJ·mol⁻¹ ($r^2 = 0.982$). This value characterizes a chemical sorption process between the compound sorbed and the sorbent (C_{11} LAS-marine sediment). This process is thermodynamically favoured, as shown by the increase of entropy with C_{11} LAS sorption (-410 J·mol⁻¹K⁻¹), and takes place spontaneously ($\Delta G < 0$). Sorption enthalpy has been calculated for LAS sorption on plastic applying the van't Hoff equation to sorption coefficients estimated from a Langmuir isotherm. The energy associated with LAS sorption on polypropylene is less than that on sediment, and this process is at the limit between physisorption and chemical sorption ($\Delta H = -60$ KJ·mol⁻¹).

A clear tendency with temperature has not been detected for C_{11} SPC sorption, and consequently the corresponding thermodynamic parameters have not been calculated. SPC association with sediment should be a labile physisorption process, considering the low sorption and high desorption rate detected.

Conclusions

The sorption of linear alkylbenzene sulfonates and of their main biodegradation intermediates, sulfophenylcarboxylic acids has been characterized in marine sediments. The C_{11} LAS sorption required 12 h to reach the steady state and 24 h for C_{11} SPC. C_{11} LAS sorption is exothermic process and consequently decreases with temperature. The presence of the carboxylic group reduces sorption on sediment, in

fact C_{11} SPC sorption is less complete and less homogeneous than for C_{11} LAS. The sorption kinetic constant is significantly higher for C_{11} LAS than for C_{11} SPC, but the desorption constant of C_{11} SPC is slightly higher than the corresponding constant of C_{11} LAS. Consequently the presence of the carboxylic group in the molecule reduces the velocity and the intensity of C_{11} SPC sorption, and favors a faster desorption than that detected for C_{11} LAS. Sorption enthalpy calculated for C_{11} LAS sorption characterizes a chemical sorption process between the compound sorbed and the marine sediment. However the energy associated with LAS sorption on polypropylene is less than that on sediment, and this process is at the limit between physisorption and chemical sorption.

The alkylic or carboxylic chain length (C_{10} - C_{13}) is correlated positively with the partition coefficient, and the effect of the carboxylic group is more significant than that of the additional methylene group. Sorption of LAS and SPC homologues (C_{10} - C_{13}) are reversible processes. Desorption of SPC homologues is almost complete, but the desorption percentage of LAS homologue decreases with alkylic chain length. Small fractions of sorbed LAS homologues could take longer to be desorbed than the times covered by this study.

Acknowledgments

This research has been supported by the Environmental and Climate Program of the European Commission PRISTINE (Contract ENV4-CT97-494) from Waste Water Cluster and by the Spanish Inter-Ministerial Science and Technology Commission "BALAS" project (CICYT, REN2001-2980-C02-01/HID).

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